

Methods of Soils Pollution Spread Analysis: Case Study of Mining and Chemical Enterprise in Lviv Region (Ukraine)

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ABSTRACT

This study is dedicated to the assessment of the heavy metal pollution of soil by determining the category of soil contamination due to the activities of mining and chemical enterprise. The X-Ray Diffraction method was used experimentally to determine the qualitative and quantitative composition of heavy metals and other inorganic elements in samples, soil pollution with heavy metals. Main sources of heavy metals in industrial waste are identified. The environmental pollution with some heavy metals (Sr, Cr, Pb, Zn, Cu, Mn) was assessed and exceeded the MPC. The ecological situation of soil contamination with heavy metals near tars on the study area territory is estimated in the category from permissible pollution to hazardous pollution. Soil near the phosphogypsum dump is classified as an acceptable, moderately dangerous, and dangerous category of soil pollution. It was established that at a distance of 20 m from the tailings the soils belong to the dangerous category of soil, closer to the tailings – to moderately dangerous. The value of the concentration coefficient indicates the activity of leaching processes ($C_C < 1$) and accumulation ($C_C > 1$) of substances in the genetic horizons of the soil. It is necessary to forecast the state of the environment in the area of influence of these enterprises to develop effective means of ensuring environmental safety.

Keywords: liquidation state, environmental monitoring, ecological changes, mining, soil pollution.

INTRODUCTION

The development of human society and the satisfaction of its needs takes place with the constant extraction and further use of natural resources. The result is significant generation and accumulation of industrial waste [Brolla and Howe 2015]. Waste management is one of the most painful problems today and is a priority in all developed countries. In Ukraine, as a result of the generation of large amounts of waste, this problem has become particularly acute [Ishchenko et al. 2018]. As a result of industrial production in areas of location of various enterprises and places of extraction of minerals, and also quite often near settlements there are the centers of the industrial desert with insignificant vegetation and even without it. The soil here is contaminated with industrial emissions, construction waste, ash from

thermal power plants, rock extracted from mines and quarries as a result of underground works, flooded with oil products, household waste, etc. In such areas, the soil is so spoiled that it loses fertility. In 2000, the mass of production waste in the world exceeded 100 billion tons; up to 30% of them are solid wastes of industry, urban and agricultural. The main mass of waste is generated at the enterprises of the following industries: mining, ferrous and nonferrous metallurgy, mechanical engineering, chemical, forestry and woodworking [Rudko et al. 2019, Kowalik et al. 2009]. These wastes pollute and change the earth's surface. The development of the mining and chemical industry leads to a deterioration in the quality of the environment. The environmental situation within the liquidated mining and chemical enterprises is one of the most tense in Ukraine. The problem of closing mining and chemical enterprises and

transforming man-made landscapes into a natural state in the context of solving priority environmental problems is relevant for Ukraine at the current stage of its development.

Today, one of the most important problems in the Lviv region is the solution of environmental problems caused by the previous production activities of mining and chemical enterprises. Ukrainian industrial enterprises pollute the biosphere by a large number of harmful substances, among which heavy metals are important negative factors.

According to the National Center of the Institute of Soil Science and Agrochemistry, today about 20% of the territory of Ukraine is contaminated with heavy metals, which negatively affects the ecological state of the environment. Excessive amounts of heavy metals in soils are a very dangerous environmental factor, the effect of which is exacerbated by the penetration of heavy metal compounds into groundwater, accumulation in plant organisms, adverse effects on soil organisms, and the cultivation of environmentally hazardous products.

The non-rehabilitated working pits edges, unliquidated quarry excavations, mine voids were

inherited, and chemical waste, unresolved issue of reclamation of disturbed lands left from the activity of the enterprises of State Enterprise (SE) “Rozdil Mining and Chemical Enterprise (MCE) “Sirka”, Yavoriv State Mining and Chemical Enterprise (SMCE) “Sirka”, SE “Podorozhnensky Rudnyk” and Stebnyk SMCE “Polimineral” (fig. 1). Due to underfunding from the state budget, the implementation of complex projects on restructuring and liquidation of mining and chemical enterprises and the implementation of urgent environmental measures in the area of their activities is not completed today [Sherameti 2015, Yelapaala 2004].

The purpose of the work is the assessment of the heavy metal pollution of soil by determining the category of soil contamination due to the activities of mining and chemical enterprises and the disposal of industrial waste.

MATERIALS AND METHODS

Soil sampling, selected in 2017, is analyzed using X-Ray Diffraction (XRD) technique. The concentration of elements in the sample was

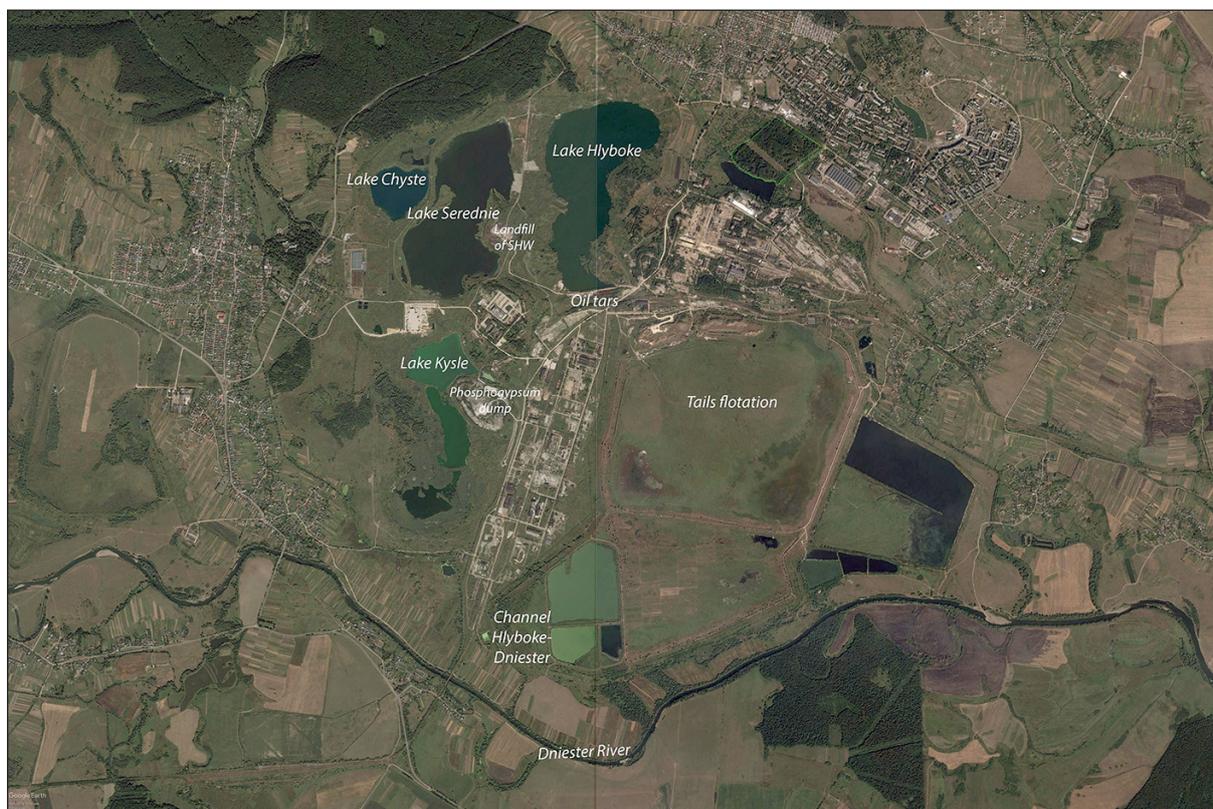


Fig. 1. Location of industrial waste on the territory of State Enterprise “Rozdil Mining and Chemical Enterprise “Sirka”

determined by X-ray spectrometry using an S2 PICOFOX Bruker X-ray spectrometer - detector type: silicon drift detector, high voltage generator: MNX 50P50 / XCC, X-ray source: metal ceramic air cooled MCB50-0.7G, X-ray optics: multilayer monochromator.

Direct sample preparation:

1. An aqueous solution of a concentrated gallium standard (100 μl) in distilled water (10 ml) was prepared.
2. To 20 ml of a gallium standard water solution was added to 1 ml of the sample and mixed well in vortex (5 seconds).
3. Prepared samples were applied to quartz media and analyzed on an X-ray spectrometer. The analysis time was 1000 seconds. The determinations were carried out in Manuel off mode - work at maximum 50W lamp power, 50 keV energy.
4. Results are expressed in units of $\mu\text{l/l}$.

Determining the characteristics of solids is important for research in geology, science, materials science, engineering and biology. Using this method determines the characteristics of crystalline materials; detection of fine-grained minerals, in particular, clays; accurate determination of the parameters of the unit cell; measuring the purity of the sample [Pohrebennyk et al. 2019, Gauglitz and Moore 2014, Pohrebennyk et al. 2016, Pohrebennyk et al. 2017].

Study Area

Soil contamination with heavy metals near industrial waste was analyzed by measuring their concentration in the soil at different distances from the landfill [Savoyskaya 2017, Kopalnia Siarki "Osiek" 2007]. The limit of toxic action of a particular heavy metal is very difficult to establish, because man-made soil pollution is usually polyelemental. Therefore, it is extremely necessary to assess the condition of soils and plants, based on the calculation of the total pollution Z_c .

The limit of toxic action of a particular heavy metal is difficult to establish because man-made soil pollution is usually polyelemental. Therefore, a sanitary and hygienic assessment of the condition of soils and plants, based on the calculation of the total pollution rate Z_c , is extremely necessary.

To estimate the level of soil pollution, you can use the total pollution index Z_c (1, 2, 3) for n considered anomalous factors, which determines the polyelement soil pollution and is calculated by the equation of Yu. Saet:

$$C_c = C_i/MPC_i \quad (1)$$

or

$$C_c = C_i/C_{bi} \quad (2)$$

where: C – the content of a certain chemical element in the soil, mg/kg; C_{bi} – background content of a certain chemical element in the soil, mg/kg; MPC – the maximum permissible concentration of the pollutant, mg/kg.

$$Z_c = (C_1/MPC_1 + C_2/MPC_2 + \dots + C_n/MPC_n) + 1 \quad (3)$$

where: Z_c – total indicator of soil contamination; C_i/MPC_i – the coefficient of concentration of the i -th chemical element in the soil sample; n – the number of chemical elements taken into account.

Assessment of the risk of soil contamination by a complex of chemical elements on the indicator Z_c is performed according to an evaluation scale, the gradation of which is developed on the basis of studying the health of the population living in areas with different levels of soil contamination (Table 1).

RESULTS AND DISCUSSIONS

The total pollution index can be determined both for all elements of one sample, and for a site area on a geochemical sample. In our case, the total pollution index at the sampling points was calculated: at a distance of 1 m, 5 m, 10 m, 20 m

Table 1. Indicative assessment scale of soil pollution hazard according to the total indicator Z_c

Category of soil pollution	Z_c	Changes in the quality of health of residents in areas of pollution
Permissible contamination	≤ 16	The lowest incidence of children and the minimum of functional abnormalities in the adult population
Moderately dangerous	17 – 32	Increasing the overall incidence
Dangerous	33 – 127	Increase in the general level and number of morbidity of children, number of children with chronic diseases, dysfunction of the cardiovascular system
Very dangerous	> 128	Increasing the incidence of children, reproductive dysfunction in women

from the tars; 1 m, 5 m, 10 m, 20 m from the phosphogypsum dump; 1 m, 5 m, 10 m, 20 m from the tailings. Since at each sampling point there are laboratory results and in depth, the average values of each element at a certain point are calculated (Table 2 and 3). According to the intensity and total indicator of pollution, one-element maps of soil pollution and distribution of geochemical association are prepared.

According to the above gradation (Fig. 2), the ecological situation of soil contamination with heavy metals near tars on the territory of the

enterprise is estimated in the range from permissible pollution to dangerous pollution. The soils are belonged to as the admissible, moderately dangerous, and dangerous category of soil pollution near the phosphogypsum dump. It was established that at a distance of 20 m from the tailings the soils belong to the dangerous category of soil, closer to the tailings – to moderately dangerous. The value of the concentration coefficient indicates the activity of leaching processes ($C_c < 1$) and accumulation ($C_c > 1$) of substances in the genetic horizons of the soil.

Table 2. The total rate of pollution in the enterprise Z_c in selected samples

Element / Pollution rate	MPC / background, mg/kg	1 m from the tars	5 m from the tars	10 m from the tars	20 m from the tars
Mn	98.24	159.37	426.91	308.65	211.36
$C_c(\text{Mn})$		1.62	4.35	3.14	2.15
Pb	1.47	18.25	25.18	5.69	10.91
$C_c(\text{Pb})$		12.41	17.13	3.87	7.42
Zn	7.20	14.10	4.82	14.84	14.18
$C_c(\text{Zn})$		1.96	0.67	2.06	1.97
Cu	2.25	6.50	11.57	4.62	9.59
$C_c(\text{Cu})$		2.89	5.14	2.05	4.26
Cr	1.23	-	13.14	17.55	-
$C_c(\text{Cr})$		-	10.68	14.27	-
Sr	1000	4338.98	-	61.48	2964.95
$C_c(\text{Sr})$		4.34	-	0.06	2.96
As	2	-	-	-	-
$C_c(\text{As})$		-	-	-	-
The total rate of pollution		19.22	33.97	20.46	14.77

Table 3. The total rate of pollution in the enterprise Z_c near the phosphogypsum dump

Element / Pollution rate	MPC / background, mg/kg	1 m from the phosphogypsum	5 m from the phosphogypsum	10 m from the phosphogypsum	20 m from the phosphogypsum
Mn	98.24	233.46	218.93	282.28	226.38
$C_c(\text{Mn})$		2.38	2.23	2.87	2.30
Pb	1.47	7.98	-	8.77	8.08
$C_c(\text{Pb})$		1.40	-	5.97	5.50
Zn	7.20	8.69	7.77	13.39	11.06
$C_c(\text{Zn})$		1.21	1.08	1.86	1.54
Cu	2.25	22.63	37.70	18.91	6.62
$C_c(\text{Cu})$		10.06	16.76	8.40	2.94
Cr	1.23	-	-	18.20	11.78
$C_c(\text{Cr})$		-	-	14.80	9.58
Sr	1000	4210.69	3437.17	2366.11	487.59
$C_c(\text{Sr})$		4.21	3.44	2.37	0.49
As	2	-	-	4.81	4.06
$C_c(\text{As})$		-	-	2.41	2.03
The total rate of pollution		15.25	20.50	32.67	18.37

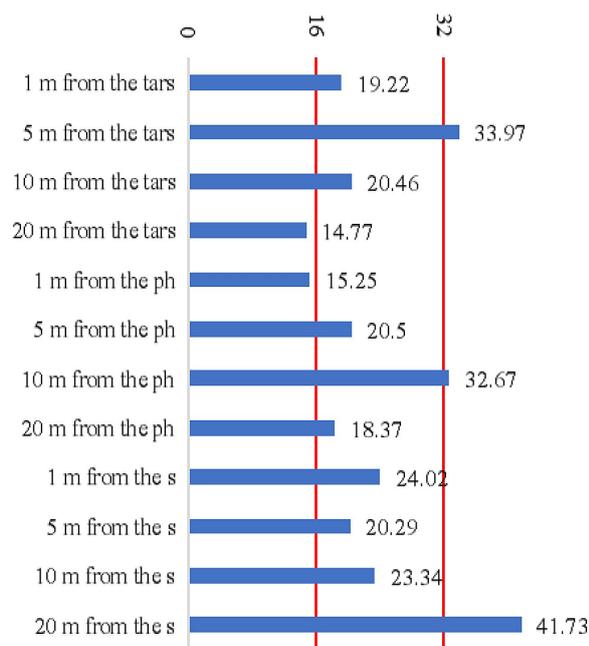


Fig. 2. The total rate of pollution in the enterprise, where ph is soil near the phosphogypsum dump, s is soil near the sulfur tailings

According to international experience, environmental protection products used in mining and chemical enterprises are unable to prevent the deterioration of environmental safety [Dartan et al. 2017, Sun et al. 2012, Pohrebennyk and Dzhumelia 2020]. To develop effective means of ensuring environmental safety, it is necessary to forecast the state of the environment in the area of influence of these enterprises [Pietrzykowski and Cieřlik 2018, Macías et al. 2017]. Monitoring should be one of the main stages of reclamation and liquidation of the mining complex [Lee et al. 2017, Bryk and Kołodziej 2009, Muravyov and Belyuchenko 2007, Medina and Silveira 2013].

Also using the total indicator of pollution Z_c in the system of ecological monitoring it is possible to determine zoning according to the level of danger of soil pollution of the territory of the mining and chemical enterprise at the stage of liquidation [Asiedu 2013, Dulewski and Uzarowicz 2008, Nita and Myga-Piatek 2006, Kelepertsis et al. 2001].

CONCLUSIONS

According to the gradation, the ecological situation of soil contamination with heavy metals near tars on the territory of the enterprise is estimated in the category from permissible pollution to

hazardous pollution. Soil near the phosphogypsum dump is classified as an acceptable, moderately dangerous, and dangerous category of soil pollution. It was established that at a distance of 20 m from the tailings the soils belong to the dangerous category of soil, closer to the tailings – to moderately dangerous. The value of the concentration coefficient indicates the activity of leaching processes ($C_c < 1$) and accumulation ($C_c > 1$) of substances in the genetic horizons of the soil. It is necessary to forecast the state of the environment in the area of influence of these enterprises to develop effective means of ensuring environmental safety.

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